Charge transfer transitions in the photoluminescence spectra of Zn1−x Me x O (Me=Mn, Ni, Co) oxide compounds

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Charge transfer transitions in the photoluminescence spectra of $Zn_{1-x}Me_xO$ (Me = Mn, Ni, Co) oxide compounds

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Crystals of $Zn_{1-x}Co_xO$ and $Zn_{1-x}Ni_xO$ are studied by photoluminescence at temperatures of 8 and 90 K. By resolving the spectra into sums of gaussian distributions and using the known positions of donor and acceptor levels of 3*d*-impurities relative to the edges of the allowed bands, the observed peaks in the photoluminescence spectra are interpreted in terms of radiative recombination through donor and acceptor levels of nickel and cobalt ions. These results are compared with previously observed features of the photoluminescence spectra of $Zn_{1-x}Mn_xO$ crystals. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4775750]

Introduction

In recent years the optical properties of manganese-doped zinc oxide have been found to differ substantially from those of other II-VI:Mn compounds. First, the optical absorption spectrum of this compound contains a broad, intense structurelesss band in the region of 2–3 eV and no lines of intra-center transitions.[1] Second, the photoluminescence (PL) spectrum of ZnO:Mn compounds have no peak in the region of 2.1 eV, which corresponds to an intra-center transition from the first excited state $^4T_1$ of the Mn^{2+} ion to the ground state $^6A_1$.[2] The reason is strong hybridization of the d-states of manganese ions with p-states of the oxygen ions. In ZnO:Mn this type of hybridization shows up more strongly because of a smaller cation-anion separation than in other II-VI:Mn compounds. An increasing degree of hybridization leads to an antiferromagnetic p-d exchange interaction. This causes the formation of a deep antibonding state in the band gap, for which localization of a hole at ions of the nearest coordination spheres is typical. As a result of interband excitation, a hole in the valence band is localized in an antibonding state and its annihilation by an electron in the conduction band shows up in the photoluminescence spectrum of ZnO:Mn crystals as a peak at an energy of 2.9 eV.[3,4]

It would be interesting to test whether strong hybridization occurs in zinc oxide crystals that have been doped with other 3*d*-elements and, if so, just how. In this paper we present data from a study of the PL spectra of $Zn_{1-x}Co_xO$ and $Zn_{1-x}Ni_xO$. We have observed photoluminescence owing to radiative transitions with charge transfer, which are essentially absent in the other II-VI:3*d* compounds. In optical absorption spectra these transitions show up as broad, intense bands which are substantially stronger than in other II-VI compounds doped with nickel and cobalt.

Experiment

PL spectra at 90 K were taken on a system with two DMR-4 monochromators (reciprocal linear dispersion 10 Å/mm in the 5 eV range). The detector was a Hamamatsu R6358-10 photomultiplier. The excitation source was a 400 W DDS-400 deuterium lamp with a continuum spectrum in the UV. The PL spectra at 8 K were recorded at the DESY synchrotron (SUPERLUMI station, Hamburg, Germany) using an ARC Spectra Pro-308i monochromator and a Hamamatsu R6358P photomultiplier with pulsed excitation. The pulse duration was 1 ns with a period of 96 ns.

Results and discussion

PL spectra of $Zn_{1-x}Co_xO$ with $x = 0.0007$ and $x = 0.007$ recorded at $T = 90$ K are shown in Fig. 1. Figure 2 shows PL spectra of $Zn_{0.993}Co_{0.007}O$ and $Zn_{0.998}Ni_{0.002}O$ taken at $T = 8$ K. The measurements at 8 K were made in order to obtain more reliable data on the luminescence of zinc oxide crystals with nickel and cobalt impurities under more intense excitation. Figures 1 and 2 show that when the temperature is lowered to 8 K the PL peak for crystalline $Zn_{0.993}Co_{0.007}O$ is observed at the same energy, 2.8 eV, as at 90 K, but the emission from deep impurity centers shows up less distinctly than for crystalline $Zn_{0.9993}Co_{0.0007}O$. In the case of nickel impurity, two luminescence peaks are observed at $T = 8$ K (Fig. 2). For a cobalt concentration $x = 0.0007$, a wide PL peak at E = 2.4 eV can be seen in Fig. 1; it is caused by radiative recombination through deep impurity centers. When the cobalt concentration is raised to $x = 0.007$, this luminescence is quenched and luminescence associated with the cobalt impurity appears, so that the peak is shifted to an energy of 2.8 eV. In addition, at the low concentration there is another peak at 3.3 eV that is not observed at the higher concentration. Thus, Fig. 1 shows that cobalt impurity is capable of suppressing the luminescence. In the PL spectra for crystalline $Zn_{0.993}Co_{0.007}O$ and $Zn_{0.998}Ni_{0.002}O$ there are peaks caused by transitions through donor and acceptor levels of the Ni^{2+} and Co^{2+} ions; these peaks correspond well to charge-transfer bands that show up clearly in the absorption spectra of these compounds. The high energy edges of the wide bands in the PL spectrum are determined by the

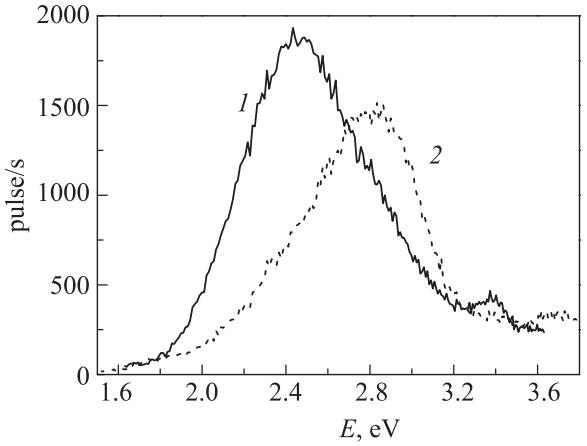

FIG. 1. PL spectra of $Zn_{0.9993}Co_{0.0007}O$ (excitation energy 4.13 eV) (1) and $Zn_{0.993}Co_{0.007}O$ (excitation energy 4.47 eV) (2) crystals for $T = 90$ K.

position of the donor (0/+) and acceptor (0/−) levels of the 3*d* impurities relative to the edges of the allowed bands. In fact, these levels are antibonding states that develop as a result of hybridization of *d*-states of the impurity ions with p-states of the ions in the near surroundings. Figure 3 shows two possible channels for radiative transitions through donor or acceptor levels. The mechanism of these transitions is the following: with interband excitation (process 1 in Fig. 3), free electrons are produced in the conduction band and holes in the valence band. Free carriers can also be formed by impurity absorption (process 2). After capture of a hole at a donor level or an electron at an acceptor level (process 3), the system can return to the ground state through electron-hole recombination. Two variants of this recombination are possible. First, it can be radiative recombination with emission of a photon (process 4) and, second, an Auger process involving a radiationless transition of a carrier with transfer of the energy of excitation to the *d*-shell (transition 5, known as DAR or Defect Auger Recombination),[5] as a result of which a 3*d*-impurity ion ends up in one of the excited states.

We now discuss the luminescence spectra of $Zn_{1-x}Co_xO$ and $Zn_{1-x}Ni_xO$ taking into account the real position of the donor (0/+) and acceptor (0/−) levels of cobalt and nickel relative to the edges of the band gaps. For this, we turn to Figs. 4 and 5, the upper parts of which show a decomposition of the PL spectra at 8 K into a series of components consisting of gaussian distributions, while the lower parts show the optical absorption spectra of these compounds from Ref. 6 and the main zero phonon lines (ZPL) of the electron absorption spectra from Refs. 7 and 8. According to Ref. 7, the donor level of cobalt is separated from the bottom of the conduction band by 2.47 eV. It is also shown thee that an acceptor level can exist in this compound, in accordance with the universal tendency that the deep levels of the 3*d* elements should be separated by approximately 3.3 eV from the peak of the valence band, i.e., near the bottom of the conduction band. Ferromagnetic ordering in $Zn_{1-x}Co_xO$ indicates the existence of such a level. The high energy edge of the gaussian component 3 of the PL spectrum of $Zn_{0.993}Co_{0.007}O$

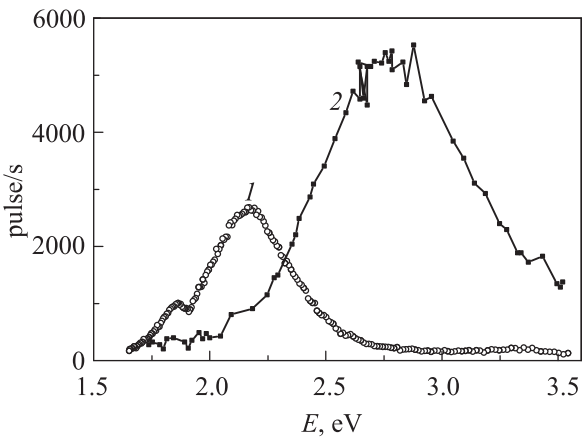

FIG. 2. PL spectra of $Zn_{0.998}Ni_{0.002}O$ (1) and $Zn_{0.993}Co_{0.007}O$ (2). The excitation energy is 6.2 eV and $T = 8$ K.

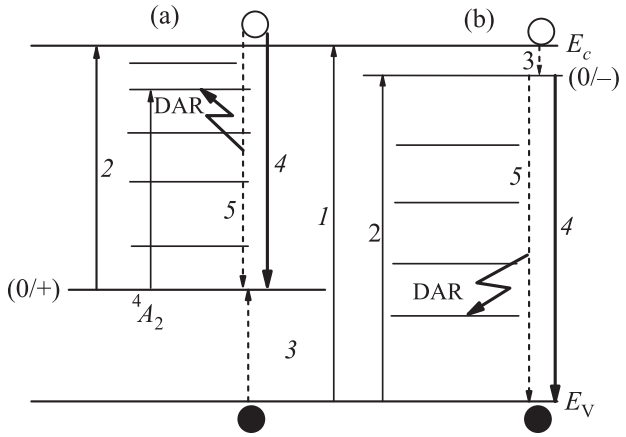

FIG. 3. Variants of radiative recombination through donor (a) and acceptor (b) impurity levels of the Co^{2+} ion (configuration d^7). Conventional notation: (●) holes, (○) electrons. (1) Interband excitation, (2) impurity absorption, (3) capture of a band carrier at an impurity level, (4) radiative recombination, (5) radiationless recombination or Auger process. A zigzag arrow indicates a transition of the Co^{2+} ion into one of the excited intracenter states.

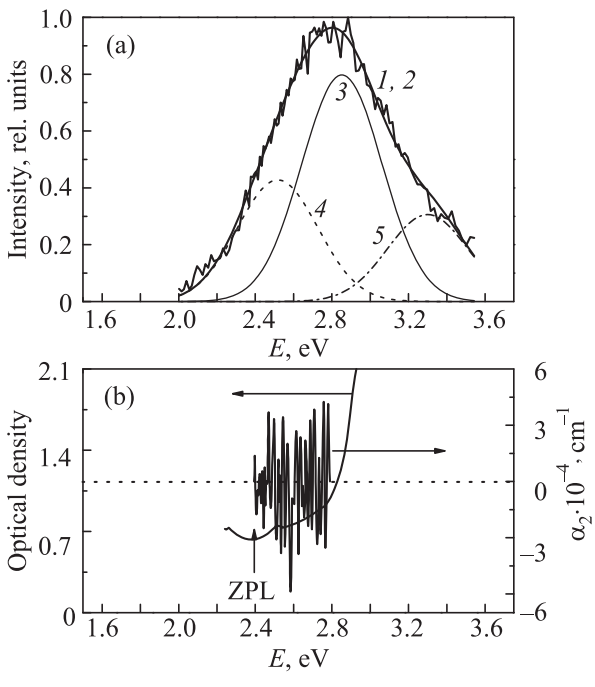

FIG. 4. (a) Decomposition of the PL spectra of $Zn_{0.993}Co_{0.007}O$ crystals at 8 K for an excitation energy of 6.2 eV into gaussian components: (1) experiment, (2) calculation; (3)–(5) gaussian components. (b) Optical absorption[6] and electron absorption[7] spectra of ZnO:Co crystals. The position of the principal zero phonon line (ZPL) is indicated.

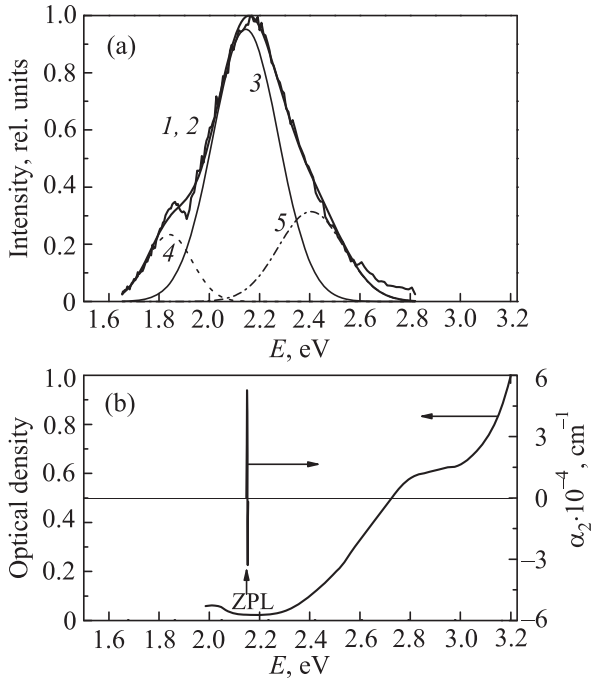

FIG. 5. (a) Decomposition of the PL spectra of $Zn_{0.998}Ni_{0.002}O$ crystals at 8 K for an excitation energy of 6.2 eV into gaussian components: (1) experiment, (2) calculation; (3)–(5) gaussian components. (b) Optical absorption spectrum[6] and principal zero phonon line (ZPL) of the electron absorption spectrum[8] of ZnO:Ni crystals.

at 8 K lies at roughly the same position (Fig. 4(a)). The gaussian 4 corresponds to emission via a deep impurity center with a maximum at 2.4 eV (curve 1 of Fig. 1). None of the gaussians had a high energy edge in the region of 2.5 eV. Thus, the photoluminescence of $Zn_{0.993}Co_{0.007}O$ with a maximum in the 2.75 eV region probably originates in an acceptor level; as shown in Fig. 3(b), the donor level makes no contribution to it. This is understandable. The probability of a transition via the donor level is considerably smaller, since a considerably larger energy must be given up upon capture of a first carrier at this level than for an acceptor level. (The latter lies very close to the bottom of the conduction band, from which it is separated by only 0.05 eV, while the donor level lies quite far from the top of the valence band, at a distance of 0.88 eV.[5]) In the case of $Zn_{0.998}Ni_{0.002}O$, on the other hand, the high energy edge of the gaussian 4 (Fig. 5(a)) lies at an energy of 2.1 eV, while the corresponding edges of gaussians 3 and 5 lie in the region of 2.6–2.8 eV. A broad photoionization band beginning roughly at an energy of 2.2 eV has been observed previously in the absorption spectrum of $Zn_{1-x}Ni_xO$.[6,9,10] The electron absorption spectrum was first recorded at the edge of this band.[8,11] The main or phonon-free line of this spectrum lies at 2.15 eV. Taking the binding energy of the donor exciton to be 50 meV, it was found that the donor level of nickel appears at a distance of 2.2 eV from the bottom of the conduction band; this level lies roughly at the same energy as on the diagram of deep states in Ref. 5. In addition, against a background of rising intensity, in the absorption spectrum of $Zn_{1-x}Co_xO$ there is a shoulder[6] in the 2.8–3 eV region. In accordance with a universal tendency in the positioning of deep levels,[5] an acceptor level of nickel can lie in this same region in ZnO. Thus, it is natural to assume that in this case there are contributions to the PL spectrum from both donor and acceptor levels of nickel, one of which causes the peak at 1.85 eV and the other at 2.18 eV (Fig. 2, curve 1). It is still not clear which belongs specifically to the donor or acceptor levels. We assume that the transition through the acceptor level takes place at a lower energy than the transition through the donor level. It is interesting to note that two peaks have also been observed, for example, in the absorption and electron absorption spectra of ZnS:Ni, with the lower energy (2.61 eV) peak corresponding to an acceptor level and the other (3.5 eV) to a donor level.[12,13]

The peaks in the PL spectra of crystalline $Zn_{1-x}Co_xO$ and $Zn_{1-x}Ni_xO$ associated with charge transfer processes are analogous in many ways with features previously observed[3,4] in the PL spectrum of crystalline $Zn_{0.99}Mn_{0.01}O$. The only difference is that, in the case of the manganese impurity, the impurity level lies in the valence band, while an antibonding state splits off from the peak of the valence band into the band gap. With nickel and cobalt impurities the donor and acceptor levels of their ions fall directly into the band gap.

Radiative transitions through donor (0/+) and acceptor (0/−) levels in zinc oxide doped with 3d impurities are more efficient because of substantial adding of band states to the d-functions. As a comparison, we note that radiative transitions with charge transfer are not generally observed in other II-VI compounds doped with Mn, Ni, or Co. This is because of a more efficient Auger process with subsequent intracenter radiation. Thus, for example, in the compound $Zn_{0.9945}Co_{0.0055}O$ an intracenter photoluminescence is observed via a $^4T_2 \rightarrow {}^6A_1$ transition, and a smooth decrease in an energy region wider than the band gap can be seen in its excitation spectrum. This difference appears to be caused by a larger fraction of *p*-states in the formation of an antibonding state in the band gap of zinc oxide, which increases the probability of a radiative transition from the conduction band into an antibonding state that has split off from the valence band.

Final clarification of the origin of the PL peaks for $Zn_{0.998}Ni_{0.002}O$ and $Zn_{0.993}Co_{0.007}O$ will require further study of these compounds by other methods. In particular, it would be very important to take photo EPR spectra for reliable identification of the character of the deep levels corresponding to the 1.85 and 2.18 eV peaks in the PL spectrum.

In sum, we have detected peaks associated with charge transfer processes in the PL spectra of $Zn_{0.993}Co_{0.007}O$ and $Zn_{0.998}Ni_{0.002}O$. The peaks appear to correspond to radiative recombination of carriers via deep donor and acceptor impurity levels.

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